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Equation of state, thermal expansivity and compressibility under the effect of high pressure

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Abstract : Some simple thermodynamic relations are derived to investigate the high pressure behaviour of solids. The relations are used to investigate the equation of state, thermal expansivity and compressibility for eight crystals from atmospheric pressure upto the structural transition pressures. A good agreement between theory and experiment suggests the validity of the present approach.

Keywords : Thermodynamic relations, high pressure behaviour of solids

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1. Introduction

The behaviour of solids under the effect of high pressure has truly developed into an interdisciplinary area which has important implications for an application in the area of Physics, Chemistry, Materials Science, Planetary Sciences, Biology, Engineering and Technology. Apart from the discovery of various novel and unexpected phenomena, high pressure research has provided new insights into the behaviour of matter [1]. These developments have also inspired significant theoretical developments. One of the most important outputs of high pressure experiments is the pressure-volume-temperature relationship of materials termed the equation of state (EOS). The isothermal EOS gives us valuable information about the change in volume under the influence of pressure at a fixed temperature and is thus related to the compression of solids. The theoretical studies of EOS at high pressure are of fundamental interest because they permit interpolation and extrapolation into the regions in which the experimental data are sparse or lacking. The EOS for solids are obtained either empirically by fitting suitable functions to the experimental data or theoretically by application of Mie-Gruneisen equation. The credit and priority for having proposed a

pressure standard on the basis of EOS for NaCl belongs to Decker [2,3]. However, this approach has been criticised by Barsch and Chang [4]. Campbell and Heinz [5] showed that the universal and Birch-Murnaghan formulations give equations of state which are in striking disagreement. The Mie-Gruneisen EOS is written as follows

$$P = -\frac{dW}{dV} + \frac{\gamma}{V} E_{\text{vib}}, \tag{1}$$

where the first term is the pressure due to the potential energy of the compressed solid at T = 0 K and the second term is due to lattice vibrations with γ and E_{vib} being the Gruneisen parameter and the lattice vibrational energy, respectively. The different forms of expressions for the potential energy give rise to different EOS. They have in common that V/V_0 is independent and P the dependent variable and that they can not be inverted because of the complicated functional form for the potential energy. It has also been discussed [6] that the derivation of Mie-Gruneisen expression for thermal (vibrational) energy is not valid when $(\delta\gamma/\delta T)_V$ is different from zero and when thermal pressure is linear with T. It has been found that at constant V, the Gruneisen ratio rapidly descends with T. Therefore, the theoretical base for the Mie-Gruneisen EOS is insecure. Thus, it is desirable to have some simple and straight-forward method for the determination of EOS and related properties. In the present work, we derive some simple thermodynamic relations and discuss their validity by predicting the variation of unit cell volume, coefficient of volume thermal expansion and compressibility under the effect of pressure from atmospheric pressure upto the structural transition pressures.

2. Thermodynamic relations

The Anderson-Gruneisen parameter corresponding to the isothermal bulk modulus B_T is defined as [7]

$$\delta_T = -\left(\frac{1}{\alpha B_T}\right)\left(\frac{\partial B_T}{\partial T}\right)_P = -\frac{1}{\alpha B_T}\left(\frac{\partial B_T}{\partial T}\right)_V - \frac{V}{B_T}\left(\frac{\partial B_T}{\partial V}\right)_T, \tag{2}$$

where α is the coefficient of volume thermal expansion, V is the volume, P is the pressure and T is the temperature. It has been discussed in the literature [7; also see for old references] that the first term in eq. (2) can be neglected as a good approximation. Thus, one can write

$$\delta_T = -\frac{V}{B_T}\left(\frac{\partial B_T}{\partial V}\right)_T. \tag{3}$$

At constant T we can write from (3)

$$\frac{dB_T}{B_T} = -\delta_T \frac{dV}{V}. \tag{4}$$

Integration (with $B_T = B_T^0$ when $V = V_0$) gives

$$\frac{B_T}{B_T^0} = \left(\frac{V}{V_0}\right)^{-\delta_T}. \tag{5}$$

Now making use of (5) we get

$$-\frac{V}{B_T^0}\frac{dP}{dV} = \left(\frac{V}{V_0}\right)^{-\delta_T}, \tag{6}$$

$$\frac{dV}{V^{\delta_T+1}} = -\frac{1}{B_T^0 V_0^{\delta_T}} dP, \tag{7}$$

which yields upon integration

$$\int_{V_0}^{V} \frac{1}{V^{\delta_T+1}} dV = -\frac{1}{B_T^0 V_0^{\delta_T}} \int_{P_0}^{P} dP \tag{8}$$

or
$$\frac{V}{V_0} = \left[1 + \frac{\delta_T}{B_T^0}(P - P_0)\right]^{-\frac{1}{\delta_T}} \tag{9}$$

or
$$\frac{V}{V_0} = \exp\left[-\frac{1}{\delta_T} \ln\left\{1 + \frac{\delta_T}{B_T^0}\left(P - P_0\right)\right\}\right]. \tag{10}$$

Eqs. (5) and (9) give

$$B_T = B_T^0\left[1 + \frac{\delta_T}{B_T^0}(P - P_0)\right]. \tag{11}$$

Now we proceed to discuss the coefficient of volume thermal expansion α as a function of P. One can also write δ_T as follows [7].

$$\delta_T \equiv -\frac{1}{\alpha B_T}\left(\frac{\partial B_T}{\partial T}\right)_P, \tag{12}$$

where
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{13}$$

The wellknown Maxwell's thermodynamic identity is

$$B_T\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{B_T}\left(\frac{\partial B_T}{\partial T}\right)_P. \tag{14}$$

By making use of eqs. (12) and (14) we get

$$\frac{d\alpha}{\alpha} = \delta_T \frac{dV}{V}. \tag{15}$$

Integration of (15) gives the following result

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_T}. \tag{16}$$

By using (9) and (16) we get

$$\alpha = \alpha_0\left[1 + \frac{\delta_T}{B_T^0}\left(P - P_0\right)\right]^{-1}. \tag{17}$$

3. Application, results and discussion

It is thus, evident that the simple thermodynamic analysis gives some useful relations which can be used to predict the effect of pressure on matter. We make use of eq. (10) to investigate the variation of unit cell volume V/V_0 under the effect of pressure P. The input data [8] required for the present work are given in Table 1. The increasing pressure decreases the unit cell volume. The calculations have been performed for eight crystals of alkali halides such as LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr and NaI because in these crystals the structural transition pressures are higher as compared with other crystals of the same family. The alkali

Table 1. Values of input data [8].

Crystal	r_0 (Å)	α_0 (10^{-4} K^{-1})	B_T^0 (10^8 pa)	δ_T	P_T (10^8 Pa)
LiF	2.013	0 999	665	6 15	1065
LiCl	2.570	1.32	297	6.88	596
LiBr	2.751	1.50	235	7.08	384
LiI	3.006	1 80	172	7.47	208
NaF	2.317	0.96	465	5.84	824
NaCl	2.820	1.19	240	5.95	283
NaBr	2.989	1.26	199	6.30	214
NaI	3.236	1.37	151	6.46	120

halides are also the most well characterized and widely studied of all solids. Typically, the alkali halides are used as a testing ground for ionic and quantum mechanical models of solids ranging from simple pair potentials to *ab initio* calculations of the equation of state. The experimental measurements of pressure-volume data are limited. Vaidya and Kennedy [9] measured the volume of some halides upto 45 k bar at room temperature using the piston-displacement method. Boehler and Kennedy [10] studied the pressure-volume relationship of LiF and NaCl using a differential length change measurement upto 32 k bar. These experimental results are included in Table 2 for the sake of comparison. The results of V/V_0 *versus* P obtained in present work are in good agreement with the experimental data supporting the validity of EOS derived thermodynamically in the present work. Eqs. (11) and

Table 2. Calculated values of V/V_o, coefficient of volume thermal expansion α in (10^{-4} K^{-1}) and isothermal bulk modulus B_T in (10^8 pa) at different pressures P in (10^8 pa). The available experimental data are given in parantheses [9 10]. The values of P_T are given in Table 1.

	LiF			LiCl			LiBr			LiI		
P	V/V_o	α	B_T	V/V_o	α	B_T	V/V_o	α	B_T	V/V_o	α	B_T
0	1	0.999	665	1	1.32	297	1	1.50	235	1	1.80	172
5	0.993 (0.993)	0.955	696	0.984 (0.985)	1.18	331	0.980 (0.981)	1.30	270	0.974 (0 973)	1.48	209
10	0.986 (0.986)	0.914	727	0.970 (0.971)	1.07	366	0.964 (0.963)	1.15	306	0.953 (0.949)	1.25	247
15	0.979 (0.979)	0.877	757	0.958 (0.958)	0 98	400	0.948 (0.946)	1.03	341	0 935 (0.927)	1.09	284
20	0.973 (0.972)	0.843	788	0.946 (0 945)	0 90	435	0.936 (0.931)	0 94	377	0.920 (0.908)	0.96	321
25	0.967 (0.967)	0.811	819	0.936 (0.934)	0.84	469	0 924 (0.916)	0.86	412	0.906 (0.891)	0.86	359
30	0.961 (0.960)	0.782	849	0.926 (0.921)	0.78	503	0.913 (0.902)	0.79	447	0.894 (0.876)	0.78	396
35	0.955 (0.954)	0.756	880	0.917 (0 911)	0.73	538	0 903 (0.899)	0.73	483	0.884 (0 862)	0.71	433
40	0.950 (0.949)	0.729	911	0 909 (0 901)	0.69	572	0 894 (0.878)	0.68	518	0.873 (0.849)	0.66	471
45	0.945 (0.945)	0.705	942	0.901 (0.891)	0.65	607	0.886 (0 868)	0.64	553	0.865 (0.837)	0 61	508
100	0.899	0.519	1280	0 840	0.40	985	0.822	0 37	943	0.799	0 34	919
200	0.843	0.351	1895	0.778	0 23	1673	0.760	0.21	1651	0 738	0.19	1666
300	0.806	0.265	2510	0 740	0.17	2361	0.722	0.15	2359	— —	—	—
400	0.778	0.213	3125	0 713	0.13	3049	— —	—	—	— —	—	—
P_T	0.679	0.092	7214	0.676	0.089	4397	0.699	0.12	2953	0.734	0.18	1725

Table 2. *(Cont'd)*

	NaF			NaCl			NaBr			NaI		
P	V/V_o	α	B_T	V/V_o	α	B_T	V/V_o	α	B_T	V/V_o	α	B_T
0	1	0.96	465	1	1.19 (1.19)	240 (240)	1	1.26	199	1	1 37	151
5	0.989 (0.989)	0.90	494	0.981 (0.980)	1.06 (1.06)	270 (268)	0.977 (0.977)	1.09	231	0.970 (0.969)	1 13	183
10	0.980 (0.980)	0.85	523	0.963 (0.963)	0 95 (0.98)	299 (299)	0.957 (0 956)	0.96	262	0.946 (0.942)	0.96	216
15	0.971 (0.971)	0.81	553	0.948 (0.947)	0.87 (0.89)	318 (319)	0 940 (0.938)	0.85	294	0.926 (0.919)	0.83	248
20	0.962 (0.962)	0.77	582	0.934 (0.932)	0.79 (0.83)	359 (357)	0.921 (0.921)	0.77	335	0.908 (0.899)	0.74	280
25	0.954 (0.954)	0.73	611	0.922 (0.919)	0.73 (0.79)	361 (361)	0 911 (0 905)	0.70	357	0.893 (0.881)	0.66	313
30	0.947 (0.946)	0.69	640	0.911 (0.907)	0.68 (0.73)	418 (415)	0.899 (0.891)	0.65	388	0.880 (0.865)	0.60	345
35	0.940 (0.939)	0.67	669	0.900 (0.895)	0.64	448	0.888 (0 878)	0.60	419	0.867 (0.851)	0.55	377
40	0.933 (0.932)	0.64	698	0 891	0.60	478	0.878 (0.866)	0.56	451	0.856 (0.836)	0.51	409
45	0.926 (0.925)	0.61	727	0 882	0.56	508	0.868 (0.855)	0.52	483	0.847	0.47	442
100	0.87	0.43	1049	0 811	0 34	835	0.797	0.30	829	0.772	0.26	797
200	0.81	0.27	1633	0.764	0 24	1190	0 729	0.17	1459	—	—	—
300	0.77	0 20	2217	—	—	—	—	—	—	—	—	—
400	0.74	0.16	2801	—	—	—	—	—	—	—	—	—
P_T	0 66	0 08	5300	0.704	0.15	1923	0 722	0 16	1547	0.753	0.22	926

(17) are used to investigate isothermal bulk modulus B_T (inverse of compressibility) and coefficient of volume thermal expansion α as a function of pressure upto the structural transition pressures. The values of α decrease with increasing pressure. The experimental data for the pressure dependence of α are available in the case of NaCl [10]. The values of B_T increase as the pressure is increased and thus the compressibility decreases by increasing the pressure. A good agreement is obtained with the available experimental data in the case of NaCl [10]. Thus, the present work is a simple and straight-forward method for investigating the properties of crystals under the effect of high pressure. The simplicity of the method makes it possible to apply it for a number of crystals.

Finally, it should be pointed out that the present approach is based on the experimental values of $\delta_T \left[\delta_T \equiv -\frac{1}{\alpha B_T}\left(\frac{dB_T}{dT}\right)_P\right]$ which are determined by measuring the temperature dependence of B_T at constant pressure [11–13]. Such values of δ_T at a constant pressure are used to investigate the pressure dependence of V/V_0, B_T and α from atmospheric pressure upto the structural transition pressures of solids.

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